

Short communication

# Ionic liquid–polymer gel electrolytes based on morpholinium salt and PVdF(HFP) copolymer

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## Abstract

New ionic liquid–polymer gel electrolytes (IPGEs) are prepared from *N*-ethyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide (Mor<sub>1,2</sub>TFSI) and poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVdF(HFP)). To investigate the effect of propylene carbonate (PC) on the ionic conductivity of the IPGEs, the preparation methods are roughly divided into two groups according to the presence or absence of PC. The ionic conductivity for each IPGE is measured with increasing temperature and changing weight ratio of Mor<sub>1,2</sub>TFSI. The results show that the ionic conductivity increases as the temperature and weight ratio of the Mor<sub>1,2</sub>TFSI increase, and that the added PC improves the ionic conductivity of the IPGEs. In addition, thermogravimetric analysis and the data from infrared spectroscopy demonstrate the thermal stability of each IPGE and the presence of PC in the polymer network. Although the IPGEs that contain PC display high conductivity ( $\sim 1.1 \times 10^{-2} \text{ S cm}^{-1}$ ) at 60 °C, they are thermally unstable.

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## 1. Introduction

Various new industrial applications of ionic liquids (ILs) have recently been considered owing to their unique electrochemical and physical properties [1–9]. In particular, a great many ILs have been studied to promote the safety and performance of systems such as solar cells, fuel cells, capacitors, and lithium batteries. Among the advantages offered by ILS are low vapour pressure, negligible flammability and high thermal stability. When the properties of high ionic conductivity and electrochemical stability occur simultaneously, these electrolytes are potential candidates for use in batteries [10–14].

Solid electrolytes are advantageous for battery construction. For example, they facilitate the production of miniaturized structures, they are safe, and they enable batteries to operate over a wide temperature range. On the other hand,

their low ionic conductivity compared with that of liquid electrolytes has been a problem. Gel electrolytes are one type of solid electrolyte that can improve conductivity by dissolving a salt into a polar liquid in a polymer network with maintenance of mechanical stability. Various mixtures of organic carbonates with cyclic and non-cyclic groups have been used as polar solvents in gel electrolytes [15]. Unfortunately, however, these solvents normally lead to a low performance and lack of safety due to the narrow electrochemical window and vapour pressure.

Fuller et al. [16,17] have developed ionic liquid–polymer gel electrolytes (IPGEs) based on hydrophilic and hydrophobic imidazolium salts and poly(vinylidene fluoride)–hexafluoropropylene copolymer (PVdF(HFP) and thereby have opened up a new IPGE field. Until now, most of IL research has been devoted to 1,3-dialkylimidazolium salts, though an enormous number of new ILs have been synthesized. The ILs based on imidazolium cations possess generally favourable properties and the abundant and useful information gathered on them is easily accessible. The products remain expensive

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and the dependence of the thermodynamic properties and electrochemical characteristics on the content of impurities needs to be continuously investigated. Furthermore, it has been reported that the imidazolium cation has a problem with respect to the chemical and electrochemical instability caused by a possible reaction with C(2) carbon. The 1-alkyl, 2-alkyl, and 3-alkyl imidazolium salts can overcome the problem, but the systems have low conductivity [14,18].

Given the above considerations, this study examines a new *N*-ethyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide-PVdF(HFP) gel electrolyte. In previous work [14], a novel *N*-ethyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide ( $Mor_{1,2}TFSI$ ) ionic liquid, was developed. Compared with imidazolium salts, the synthesis and purification processes of  $Mor_{1,2}TFSI$  are both easy and simple. In addition, the overall reaction time is short, and the cost of raw materials is cheap. To investigate the effect of propylene carbonate (PC) on ionic conductivity, the IPGEs have been prepared by using two methods that depend on the presence or absence of PC. Thermogravimetric analysis (TGA) and infrared spectroscopy are used to determine the thermal stability and to check the presence of PC. Ionic conductivity is measured in relation to changes in temperature and the concentration of  $Mor_{1,2}TFSI$  and PC.

## 2. Experimental

### 2.1. Synthesis of $Mor_{1,2}TFSI$

Scheme 1 shows the synthesis mechanism of  $Mor_{1,2}TFSI$ . The  $^1H$  NMR and FAB mass spectra were recorded on a Bruker DMX 600 MHz NMR spectrometer and FAB mass JMS-HX110A, respectively. The possible presence of residual  $Br^-$  was examined by a precipitation test of  $AgNO_3$  and ionic chromatography by means of the system: Bio-LC DX-300 (Dionex, Sunnyvale, CA, USA); detector: suppressed conductivity (PED2); column: ICsep AN300 with ICsep ANSC guard.

#### 2.1.1. *N*-ethyl-*N*-methylmorpholinium bromide ( $Mor_{1,2}Br$ )

Under vigorous stirring, 147 g (1.35 mol) of 1-bromoethane was added dropwise to a solution of 101 g (1 mol) of 4-methylmorpholine in 200 ml of acetonitrile through which nitrogen was bubbled. The mixture was stirred at 60 °C for 5 h. The molten salt was then placed in a freezer at -20 °C. The acetonitrile was decanted from the solids and recrystallized from acetone to yield white crystalline solids, which were dried under vacuum at 30 °C to give 190 g of product for a yield of 90%.

#### 2.1.2. *N*-ethyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide ( $Mor_{1,2}TFSI$ )

The 29 g (0.1 mol) of  $LiTFSI$  was added to 21 g (0.1 mol) of  $Mor_{1,2}Br$  in 150 ml of dichloromethane. The mixture was

stirred for 1 day, and the  $LiBr$  was filtered from the reaction mixture. The resulting ionic liquid was stirred with activated charcoal for 12 h, and the IL was then passed through a neutral aluminium oxide and silicagel columns to give a colourless IL that was dried under vacuum at 40 °C for more than 12 h to give 28 g of the product for a yield of 80%.

$^1H$  NMR ( $D_2O$ ,  $\delta/ppm$  relative to TMS): 4.08 (s, 4H), 3.59–3.50 (m, 6H), 3.19 (s, 3H), 1.41 (t, 3H). FAB MS:  $m/z = 130[Mor_{1,2}]^+$ .  $Br^-$  content: no precipitation of  $AgBr$  and not detected by ion chromatography.

### 2.2. Preparation of ionic liquid–polymer gel electrolyte

Scheme 2 shows two different preparations of the  $Mor_{1,2}TFSI$ -PVdF(HFP) gel polymer electrolyte.

#### 2.2.1. Preparation of the $Mor_{1,2}TFSI$ -PVdF(HFP) gel electrolyte

The PVdF(HFP) (Atofina) was Kynar flex 2801-00.  $Mor_{1,2}TFSI$  and PVdF(HFP) copolymer were mixed with acetone for 24 h. This mixture was poured into a flat Petri dish and a doctor blade was used to form a thin and uniform film. The acetone in the mixture in the Petri dish was then evaporated for 24 h at an ambient temperature.

#### 2.2.2. Preparation of $Mor_{1,2}TFSI$ -PVdF(HFP)-PC gel electrolyte

PVdF(HFP) copolymer,  $Mor_{1,2}TFSI$  and PC were mixed thoroughly with acetone completely for 24 h. This mixture was poured into a flat Petri dish, and the acetone in the mixture in the Petri dish was then evaporated for 24 h at an ambient temperature.

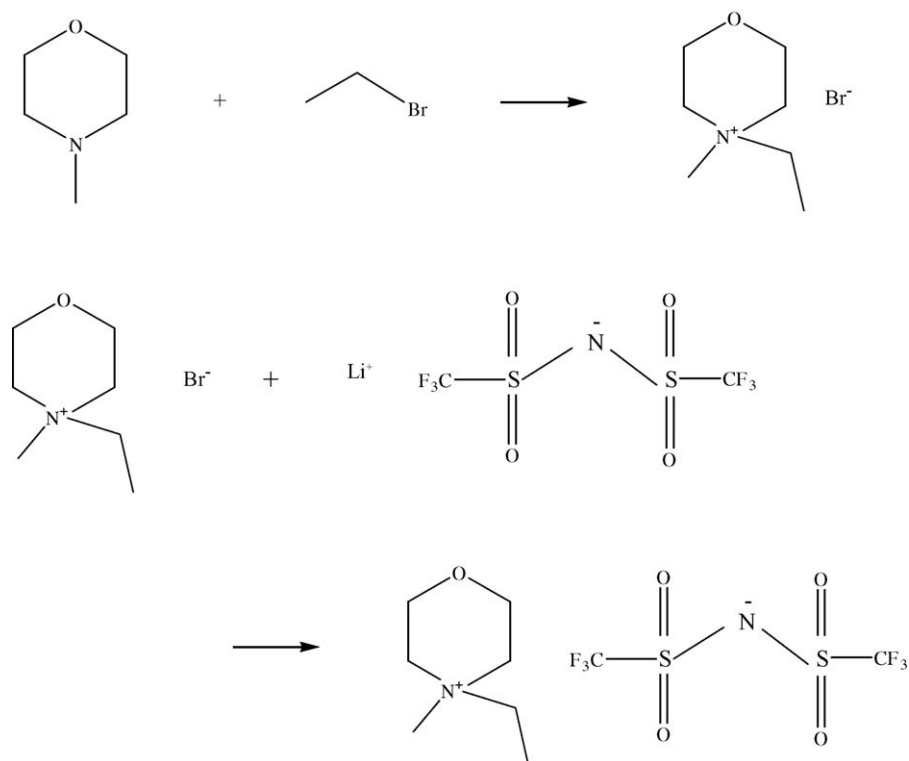
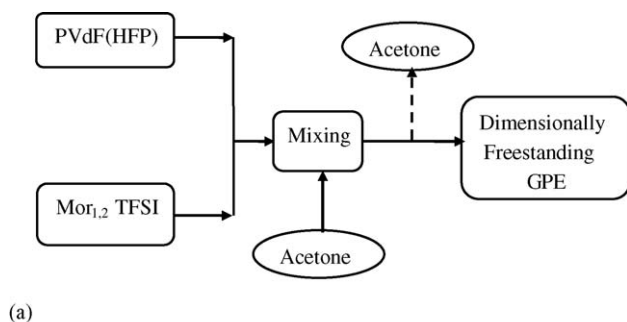
### 2.3. Apparatus and procedure

#### 2.3.1. Ionic conductivity

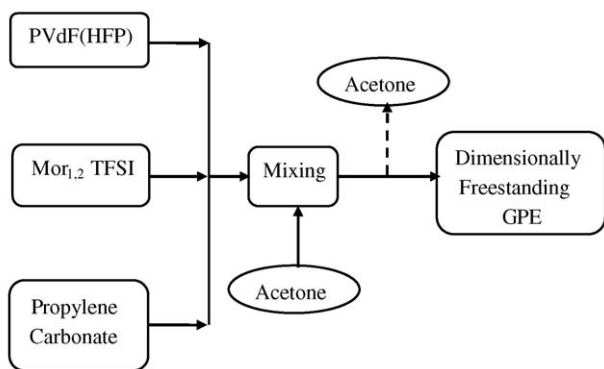
Solid films were sandwiched between two stainless-steel (SS) electrodes. The ionic conductivity of the electrolyte films was measured by means of complex impedance analysis with the aid of a Solartron 1260 Impedance/Gain-Phase Analyzer and a 1287 Electrochemical Interface coupled to an IBM computer over a frequency range of 100 Hz to 1.8 MHz. An ac perturbation of 10 mV was applied to the cell. The real and imaginary parts of the complex impedance were plotted, and the ionic conductivity was calculated from the bulk resistance ( $R_b$ ) found in the complex impedance diagram.

#### 2.3.2. Thermal analysis: thermogravimetric analyzer (TGA)

Thermal analysis and the decomposition temperature of the gel polymer electrolytes were detected using a TA instrument Thermogravimetric Analyzer (TGA) Q500. After loading samples of the IPGE in flat platinum pans, the measurements were taken under nitrogen at a heating rate of 10 °C  $min^{-1}$ .

Scheme 1. Synthesis of Mor<sub>1,2</sub>TFSI.

(a)



(b)

Scheme 2. Two different preparations of Mor<sub>1,2</sub>TFSI-PVdF(HFP) gel polymer electrolyte: (a) using only acetone, (b) using both acetone and propylene carbonate.

### 2.3.3. Infrared spectroscopy

Infrared spectroscopy (FT-IR) spectra were recorded in the absorption mode with a Bomem-MB 100 FT-IR spectrometer, which covered a range from 400 to 4000 cm<sup>-1</sup>.

## 3. Results and discussion

Mor<sub>1,2</sub>TFSI was synthesized according to our previous report [14]. No impurities of anions were detected by a precipitation test of AgNO<sub>3</sub> or by ionic chromatography. The IPGEs were prepared via the two different methods. Scheme 2a gave a free-standing IPGE that was prepared by using only acetone as a solvent. This process simplified the overall preparation of the IPGEs because only one solvent was used and the acetone could be easily and completely eliminated. In Scheme 2b, PC was added to the IPGE with acetone at the first step of the preparation process. The PC gives rise to two main phenomena: it facilitates the mixing of the IL and the polymer and it improves the ionic conductivity of the IPGE. The weight ratios of the components that formed the five IPGES are listed in Table 1.

The ionic conductivity was determined by means of a Solatron 1260A frequency response analyzer (FRA) in a temperature range of 30–60 °C. Arrhenius plots of the ionic conductivity of each IPGE at different temperatures are given in Figs. 1–4. The ionic conductivity of all IPGEs increases as the temperature and weight ratio of the ILs increase.

While the ionic conductivity of IPGE1 has a low value of 2.5 × 10<sup>-5</sup> S cm<sup>-1</sup> at 30 °C, the conductivity of IPGE3

Table 1  
Weight ratio of each component forming IPGE

	Weight ratio of PVdF(HFP) vs. Mor <sub>1,2</sub> TFSI		Weight ratio
	PVdF(HFP) (g)	Mor <sub>1,2</sub> TFSI (g)	
IPGE1	0.5077	0.5207	1:1
IPGE2	0.5024	1.0031	1:2
IPGE3	0.5029	1.5238	1:3
Weight ratio of (PVdF(HFP) + Mor <sub>1,2</sub> TFSI) vs. PC			
	Components	Weight ratio between polymer and IL (wt.% of PC)	
IPGE 1-21	IPGE1 + PC	1:1 (21 wt.%)	
IPGE2-31	IPGE2 + PC	1:2 (31 wt.%)	

reaches approximately  $8.0 \times 10^{-4} \text{ S cm}^{-1}$  at  $30^\circ\text{C}$ , as shown in Fig. 1. The data in Figs. 3 and 4 indicate that the presence of PC gives rise to an outstanding increase in ionic conductivity. At  $60^\circ\text{C}$ , the ionic conductivities of IPGE1-21 and IPGE2-31 surge to  $6.3 \times 10^{-3}$  and  $1.1 \times 10^{-2} \text{ S cm}^{-1}$ , respectively. This result confirms that PC is one of the best organic carbonates: its high dielectric constant and low vis-

cosity are favourable for dissolving and separating the IL in the polymer. Moreover, PC normally guarantees high ion conduction.

The TGA was conducted with the TA instrument Q500 coupled with an IBM computer. The temperature range of the trace was  $30\text{--}600^\circ\text{C}$  with a  $10^\circ\text{C min}^{-1}$  heating rate under  $\text{N}_2$  ambient. The degradation curves for Mor<sub>1,2</sub>TFSI in the polymer matrix are given in Fig. 5. It is found that

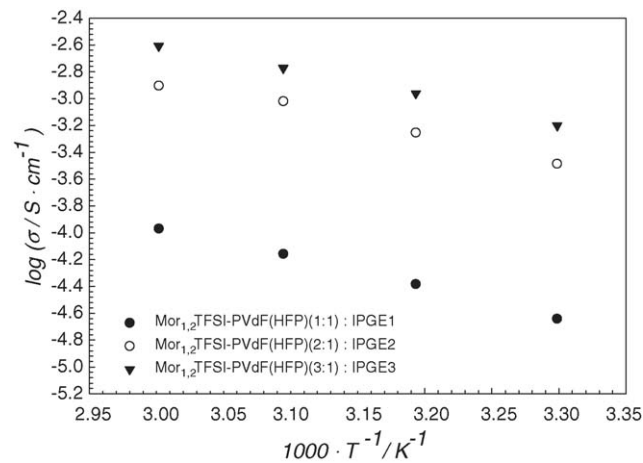


Fig. 1. Ionic conductivities of IPGE1, 2, and 3.

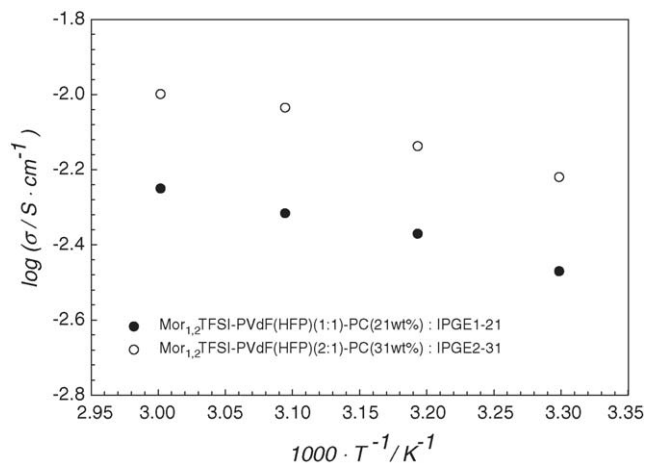


Fig. 2. Ionic conductivities of IPGE1-21 and 2-31.

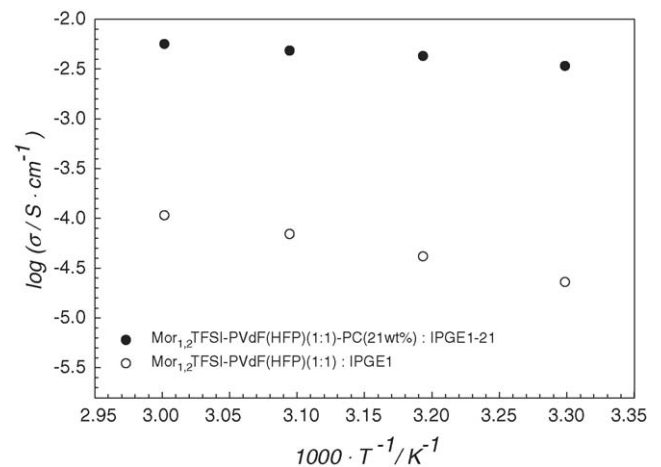


Fig. 3. Ionic conductivities of IPGE 1 and 1-21.

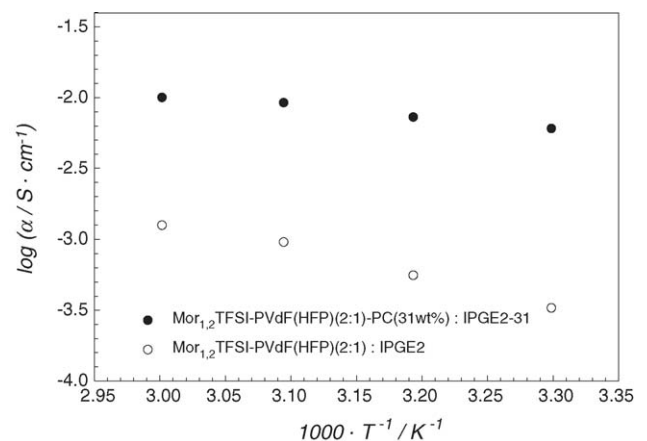


Fig. 4. Ionic conductivities of IPGE 2 and 2-31.

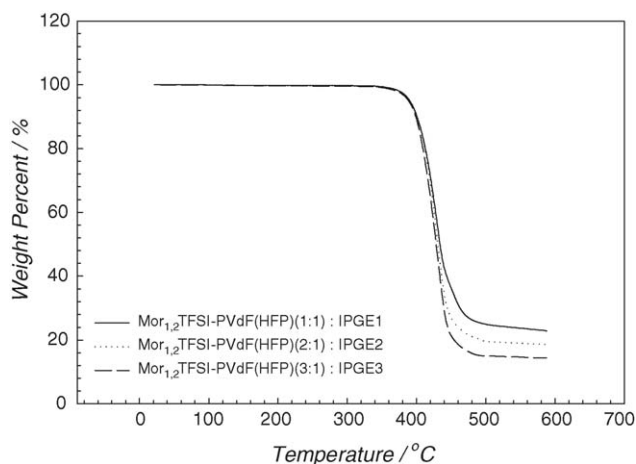


Fig. 5. TGA diagram of IPGE 1, 2, and 3.

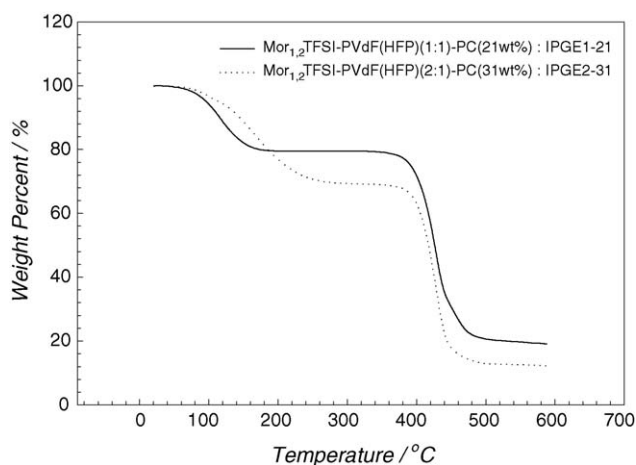


Fig. 6. TGA diagram of IPGE 1-21 and 2-31.

IPGEs that use  $\text{Mor}_{1,2}\text{TFSI}$  without any solvent are stable up to approximately  $400^\circ\text{C}$ . Furthermore, the undetectable vapour pressure of  $\text{Mor}_{1,2}\text{TFSI}$  secures the high thermal stability of IPGEs. The TGA curves for PC and  $\text{Mor}_{1,2}\text{TFSI}$

for IPGE1-21 and IPGE 2-31, respectively, are presented in Fig. 6. The vaporization curves of PC are observed below  $100^\circ\text{C}$ . Although PC is known as an organic solvent with a high boiling point ( $242^\circ\text{C}$ ), the PC evidently vapourizes and can cause hazardous conditions. On the other hand, the acetone is completely vapourized merely by exposure to an ambient condition for 24 h. No acetone is observed in the curve for IPGE1, see Fig. 7. The infra-red absorbance of IPGE 1-21 at near  $1800\text{ cm}^{-1}$  represents the characteristic  $\text{C}=\text{O}$  stretching bands of PC.

#### 4. Conclusions

New IPGEs have been developed from  $\text{Mor}_{1,2}\text{TFSI}$  and PVdF(HFP). Each IPGE is prepared by changing the concentration of the IL or PC. The ionic conductivity of the IPGEs increases as the temperature and concentration of  $\text{Mor}_{1,2}\text{TFSI}$  increases. In addition, PC enhances the ionic conductivity of IPGE, and the highest ionic conductivity, namely  $1.1 \times 10^{-2}\text{ S cm}^{-1}$  at  $60^\circ\text{C}$ , is found with IPGE2-31. Besides showing the presence of PC, the IR spectra demonstrate a complete elimination of acetone. The TGA data show that the IPGE composed of an IL and polymer has high thermal stability. On the other hand, for the IPGE composed of IL, PC, and polymer, the vapourization curve of PC is observed from a low temperature. The IPGE with PC has high ionic conductivity, though there is an indication of a problem of PC vapourization below  $100^\circ\text{C}$ .

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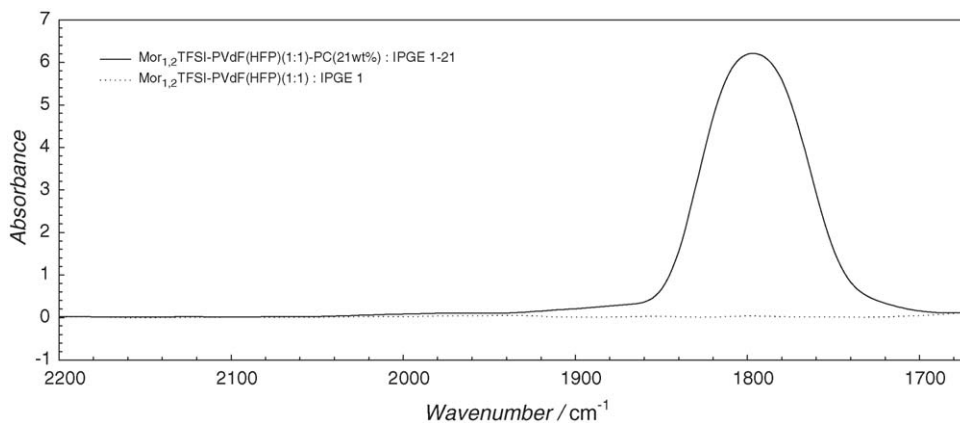


Fig. 7. IR spectra of IPGE 1 and 1-21.

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